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(54) Title of Invention: MANUFACTURE OF ORGANIC SOLVENT  
BATTERY

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## SPECIFICATION

### 1. Title of Invention

MANUFACTURE OF ORGANIC SOLVENT BATTERY

### 2. Claim

Manufacture of organic solvent battery is characterized by cathode composite paste formed by adding polyacrylic acid thickener and dispersion of PTFE binder to mixture of manganese dioxide as cathode active material and graphite conducting agent, drying, and compressing to form cathode; said cathode, lithium anode active

material, and organic solvent electrolytic solution are combined,

wherein sodium impurity in said manganese dioxide is neutralized so it's under 0.1 weight %, and said cathode composite paste is prepared at pH 5 - 10 and dried to form cathode.

### 3. Detailed Explanation of Invention

[Object of Invention]

(Field of Industrial Utility)

This invention concerns manufacture of cathode of organic solvent battery with manganese dioxide as cathode active material.

(Past Technology)

In recent years, organic solvent batteries with electrolytic solution (electrolytes dissolved in organic solvent such as PC and DME) are being widely used in electronic machines. Among these, there's been great demand for organic solvent batteries which are extremely thin and, on top of that, highly reliable accompanying the miniaturization and slimming of electronic machines such as pocket calculators, electronic watches, IC cards, etc..

Hitherto, manganese dioxide (for use as cathode in organic solvent battery) was manufactured by sintering manganese dioxide ore, treating with sulfuric acid, then electrolyzing. Resulting manganese dioxide was treated with sodium hydroxide in the final process to neutralize sulfuric acid and to control pH. Cathode utilizable in organic solvent battery was manufactured by adding polyacrylic acid thickener and PTFE binder to mixture of said manganese dioxide and graphite conducting agent, made into cathode composite paste, dried, then compressed.

(Problems Invention Proposes to Resolve)

However, if manganese dioxide manufactured by said electrolysis method is used as cathode active material of organic solvent battery, there's marked deterioration of capacity during storage (especially high temperature storage). Probable cause: sodium impurity is present because sodium hydroxide was used in the neutralization and pH adjustment in the final stage during manufacture of manganese dioxide. Said sodium goes into electrolytic solution inside the battery, depositing as sodium on lithium anode surface during storage, impeding reaction of lithium during discharge, and leading to deterioration of discharge capacity.

This invention resolves said problems and offers organic solvent battery with superior storage and discharge performances by using manganese dioxide with less than 0.1 weight % sodium impurity content, by preparing cathode composite paste at pH 5 - 10 in cathode manufacturing process, and by using lithium hydroxide in pH

adjustment of cathode composite paste .

[Composition of Invention]

(Means to Resolving Problems)

This invention concerns manufacture of organic solvent battery by forming cathode composite paste by adding polyacrylic acid thickener and dispersion of PTFE binder to mixture of manganese dioxide as cathode active material and graphite conducting agent, drying, and compressing to form cathode; said cathode, lithium anode active material, and organic solvent electrolytic solution are combined. Sodium impurity in said manganese dioxide is neutralized to under 0.1 weight %, said cathode composite paste is prepared at pH 5 to 10, and dried to form cathode.

Manganese dioxide utilizable as active material of this invention is preferably manufactured without mixing in sodium: i.e., manganese dioxide using neutralizing agent such as ammonia instead of sodium hydroxide during neutralization and pH control can be adequately used as active material containing less than 1.0 weight % sodium impurity, the original content in manganese dioxide ore.

During manufacture of cathode composite paste using said manganese dioxide, pH is preferably 5 - 10. Under pH 5, discharge capacity is diminished from non-uniformity of manganese dioxide reaction during discharge due to non-uniform mixing of graphite conducting agent and manganese dioxide caused by inadequate functioning of acrylic acid as thickener of cathode composite paste. Over pH 10, cathode composite paste becomes hard and can't be uniformly applied to cathode terminal of thin battery.

Lithium hydroxide is preferably used for pH adjustment during preparation of said cathode composite paste: Because pH adjusting reagent remains in the final cathode, for such things as sodium hydroxide (being a different metal from that of lithium anode), there's the risk of capacity deterioration from precipitation of sodium, etc., on lithium surface during storage. There's a possibility of capacity deterioration by using lithium hydroxide since it has the same element as lithium anode.

(Operation)

This invention offers organic solvent battery with superior discharge and storage performances by using manganese dioxide with less than 0.1 weight % sodium impurity in cathode active material, adjusting pH of cathode composite paste using said manganese dioxide within 5 - 10, and preferably using lithium hydroxide for said pH adjustment.

At pH 5 - 10, dispersion of thickener is accelerated in said paste; because a small amount of thickener gives required viscosity, conductivity is improved; if lithium hydroxide is used

to adjust pH, corrosion of lithium anode due to impurities can be reduced.

(Example)

Invention will be explained with example:

Densely viscous cathode composite paste was manufactured by mixing aqueous dispersion of PTFE (2 weight %) and polyacrylic acid (1 weight %) with mixture of manganese dioxide (90 weight % with 0.05 weight % sodium impurity) and graphite (10 weight %), using ammonia for neutralization and pH adjustment during the manufacture of manganese dioxide, and adding lithium hydroxide after paste is prepared to pH 6.

Said cathode composite paste was applied on top of substrate sheet to a fixed shape, drying, then compressing into cathode shaped body (1) (outer dimensions 20 X 20 mm, thickness 0.3 mm).

Cathode shaped body (1) was dried (250°C, 3 hours) then placed on cathode terminal plate (5) made of stainless steel (outer dimensions 35 X 35 mm, thickness 0.03 mm). Anode was lithium (3) pressed/adhered to anode terminal plate (6), together with said cathode and interposing separator (2) were layered to oppose each other and peripherally sealed with insulator (4) to give flat-type organic solvent battery A of this invention.

#### Comparison Example

Battery B was manufactured identical to battery A except said cathode composite paste was prepared with pH 4.

#### Past Example

Battery C was manufactured identical to battery A except manganese dioxide was used containing 0.2 weight % sodium impurity after using sodium hydroxide for neutralization and pH adjustment in the electrolysis synthesis of said manganese dioxide; pH was not adjusted during manufacture of cathode composite paste.

Figures 2 and 3 (Terminal Voltage vs. Continuous Time) show discharge curves of respective kinds of batteries (100 each) continuously discharged (20°C, 30 Kohms) and after storage (60°C, 30 days, discharged at 20°C, 30 Kohms), respectively.

Results: Beginning discharge of Comparison battery B (pH adjusted to 4 during preparation of cathode composite paste) was unsatisfactory but satisfactory for Example battery A. Capacity deterioration was conspicuous after storage (60°C, 30 days) especially for Past battery C using manganese dioxide containing sodium impurity (0.2 weight %, neutralized with sodium hydroxide during manufacture of manganese dioxide). Result: sodium precipitated on lithium anode surface.

## [Results]

This invention has obtained notable results improving storage and maintaining discharge performances by using cathode manufactured using manganese dioxide as active material with less than 0.1 weight % sodium impurity and adjusting pH to 5 - 10 after preparation of cathode composite paste.

### 4. Brief Explanation of Diagrams

Figure 1 is a cross sectional drawing of flat-type organic solvent battery made according to this invention; Figure 2 is continuous discharge graph immediately after manufacture at 20°C, 30 Kohms; Figure 3 is Figure 2 after storage (60°C, 30 days).

